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(19) (CA) **CANADIAN PATENT** (12)

(54) Use of Morpholine Neutralized Phosphate and
Thiophosphate Esters as Ethylene Furnace Anti-Coking
Antifoulants

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(73) Granted to Naico Chemical Company
U.S.A.

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Canada

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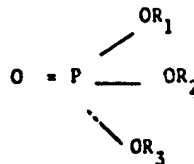
Weinland, in United States 4,105,540, describes the use of phosphorus containing compounds as anti-foulants in ethylene cracking furnaces.

Specifically, this Weinland patent, discloses that phosphate and phosphite mono and diesters in small amounts function as anti-foulant additives in ethylene cracking furnaces which are subjected to elevated temperatures from about 500° - 1700°F. These furnaces produce material that deposits and accumulates upon furnace surfaces including furnace coils and transfer line exchangers and fouls these surfaces leading inevitably to plant shutdown and expensive maintenance. The anti-foulants of the Weinland patent inhibit and suppress this fouling and also help to clean up previously fouled furnace surfaces.

The invention disclosed in United States 4,105,540 is generally described in the following way: -

"This invention entails an improved process for reducing the fouling tendencies experienced in ethylene cracking furnaces including the formation of coking and polymer deposition on furnace coils and transfer line exchangers. The treatment is effective over the temperature range 500° - 1700°F. which are found in ethylene cracking furnaces.

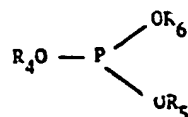
"The method involves treatment of feed stock with at least 10 ppm and, preferably 25 - 100 ppm of the phosphorus ester anti-foulants described below. In addition, it is preferred that plant equipment surfaces be pretreated with these compounds in the absence of the feed stock. The phosphite ester compounds employed in this invention are characterized by the general formula:



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where R_1 , R_2 , and R_3 are each individually selected from the group consisting of hydrogen, addition complexes of hydrogen with amines, alkyl, aryl, alkaryl and cycloalkyl, alkenyl, and aralkyl, and provided that in any given such phosphate ester at least one and not more than two of each of R_1 , R_2 , and R_3 are hydrogen or an addition complex of hydrogen with an amine.

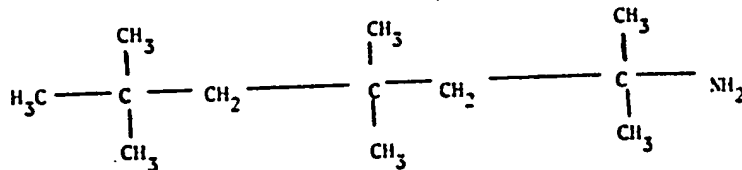
"The phosphite ester compounds employed in this invention are characterized by the general formula:



10 where: R_4 , R_5 , and R_6 are each individually selected from the group consisting of hydrogen, addition complexes of hydrogen with amines, alkyl, aryl, alkaryl and cycloalkyl, alkenyl, and provided that in any given such phosphite ester at least one and not more than two of each of R_1 , R_2 , and R_3 are hydrogen or an addition complex of hydrogen with an amine."

The preferred amine neutralized phosphate and phosphite mono and di esters are neutralized with fatty amines with a preferred amine being the material Primene 81-R, which is described in United States 4,105,540 as follows:

"The primary constituent of 'Primene 81-R' is reported to be:



20 "The primary constituent of 'Primene JM-T' is reported to be essentially the same structure as 'Primene 81-R,' but with 22 carbons. 'Primene' is a trademark of the Rohm & Haas Company for its brand of tertiary alkyl primary amines."

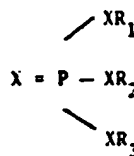
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Experience has shown that the phosphate and phosphite esters described above which have been neutralized with fatty amines such as Primene 81-R when used over prolonged periods of time in ethylene furnaces while providing anti-fouling protection do not provide corrosion protection.

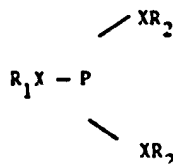
It would be a benefit if it were possible to provide anti-foulant compositions having effectiveness of those described in United States 4,105,540 yet would also provide corrosion protection when used over prolonged periods of time.

10 This invention provides an improved method of reducing fouling and corrosion in ethylene cracking furnaces using petroleum feedstocks, which comprises treating the petroleum feedstock with at least 10 ppm, and preferably 25 - 200 ppm, of a compound chosen from the group consisting of phosphite esters, phosphate esters, thiophosphite esters, thiophosphate esters and mixtures thereof, said esters being represented by Formulae I and II below:

Formula I



Formula II



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In the above formulae, X equals S or O, and R_1 , R_2 , and R_3 are each independently selected from the group consisting of hydrogen, morpholine, alkyl, aryl, alkaryl, cycloalkyl, alkenyl, and aralkyl, provided that at least one, and not more than two, of each R_1 , R_2 , and R_3 are morpholine. When the term morpholine is used herein and in the claims, it means the morpholine salt group.

Specific examples of compounds falling under the above formulas and which represent preferred species of the invention are the morpholine salts of:

- 10
- (1) a blend of the mono and di isooctylthiophosphate ester;
 - (2) a blend of the mono and di isooctylphosphate ester; and
 - (3) di n-butylphosphite.

A more detailed description of these phosphite, phosphate and thiophosphate compounds and their methods of manufacture are disclosed in United States 4,105,540.

To illustrate the advantages of the invention, the following are presented by way of Examples.

Examples

Example 1

20 A commercial ethylene plant was treated with an organo phosphorus Primer 81-R anti-foulant of United States 4,105,540. The treatment successfully prevented fouling of the furnace coils and transfer line exchangers. After several months had passed, evidence of corrosion was observed.

Example 2

A morpholine neutralized phosphate ester was developed to overcome the potential corrosion problem.

The experimental procedure consisted of placing the compound to be tested along with water and a heavy aromatic naphtha into a laboratory autoclave.

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The mixture was heated to 160°C and held at that temperature for 6 hours.

Using the above experimental technique, the following morpholine salts were compared against a commercial product of the Weinland patent:

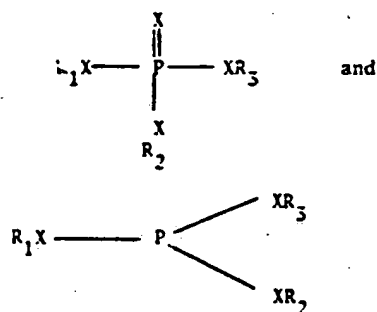
- (1) a blend of the mono and di isooctylthiophosphate ester;
- (2) a blend of the mono and di isooctylphosphate ester; and
- (3) di n-butylphosphite.

In all instances, the compositions of the invention substantially reduced corrosion, which corrosion was evidenced when the Weinland products were run.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An improved method of reducing fouling and corrosion in ethylene cracking furnaces using petroleum feedstocks, comprising treating the petroleum feedstock with at least 10 ppm of a compound chosen from the group consisting of phosphite esters, phosphate esters, thiophosphite esters, thiophosphate esters and mixtures thereof, said esters being characterized by the formulas:



where X equals S or O, and R_1 , R_2 , and R_3 , are each independently selected from the group consisting of hydrogen, morpholine, alkyl, aryl, alkaryl, cycloalkyl, alkenyl, and aralkyl, provided that in at least one, and not more than two, of each R_1 , R_2 , and R_3 are morpholine.

2. The method of Claim 1 where the ester is a blend of the mono and di isooctylthiophosphate ester.
3. The method of Claim 1 where the ester is a blend of the mono and di isooctylphosphate ester.
4. The method of Claim 1 where the ester is di n-butylphosphite.
5. The method of Claim 1 where from 25 to 200 ppm of the ester is used.

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PATENT AGENTS

